Solvation of the Halogen Acids in *N*-Methylpropionamide

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Summary Thermodynamic studies of the halogen acids in *N*-methylpropionamide reveal an unusual dependence of the ion–solvent interactions on anionic size.

ELECTROLYTE solutions in solvents of high relative permittivity (ϵ_r) show some ill understood characteristics. To supplement the data on such systems[1] we have carried out e.m.f. studies on cell (I) in *N*-methylpropionamide (NMP, $\epsilon_r = 176$).

$$\mathrm{H_2,Pt} \;|\; \mathrm{HX}, (m) \;|\; \mathrm{AgX{-}Ag}$$
$$\text{(I)};\ \mathrm{X = Cl, Br, or\ I}$$

Pure NMP is obtained without difficulty compared to other amides of high ϵ_r, and the acid solutions are all stable and show strong electrolyte behaviour. (This is confirmed by our own and other[2] conductance measurements; the conductances are in the usual order HI > HBr > HCl). The behaviour of the electrodes was satisfactory, and enabled cell e.m.f.s (E) to be reproduced to within 0·2—0·4 (HBr, HI) or 0·1 mV (HCl). The results for HCl agreed well (±0·1 mV) with those of Etz and Bates[3] in the range 0·002—0·1 *m*, but our values extend to greater dilutions and are preferred for extrapolation purposes.

We obtained values of the standard molal e.m.f. (E°_m) from extrapolation of E values in the concentration range m = 0·001—0·1, preferring to use simple plots of E' ($= E + 2\,RT/F \ln m$) against $m^{\frac{1}{2}}$. The uncertainties in E^0 values from this procedure (±1—2 mV) could not be convincingly reduced even with the use of several different extrapolation methods, but the errors are not large enough to affect general conclusions concerning the anionic solvation.

Values of the free energy of transfer ΔG°_t ($\mathrm{H_2O \rightarrow NMP}$) were calculated from the E_m values and are presented in the Table. The ΔG°_t values for $\mathrm{H^+Br^-}$ and $\mathrm{H^+I^-}$ are among the first known negative ones for transfer of an electrolyte from water to a solvent of high ϵ_r, also found for HBr and HI in formamide.[4] The favourable transfer implies stronger net interactions in NMP, and is unexpectedly in qualitative agreement with classical electrostatic theory. The transfer is favoured, however, in the order $\mathrm{I^- > Br^- > Cl^-}$, which is in the opposite sense to the ionic-size dependence predicted by Born's theory, and resembles the anomalous behaviour for transfers of cations to methanol–water mixtures.[5]

TABLE. Standard e.m.f.s and free energies of transfer for halogen acids ($\mathrm{H_2O \rightarrow NMP}$)

	$E^\circ_m(\mathrm{H_2O})/\mathrm{V}^a$	$E^\circ_m(\mathrm{NMP})/\mathrm{V}$	$\Delta G^\circ_t/\mathrm{kJ\ mol^{-1}}{}^b$
HCl	0·2224	0·1755[c]	$4{\cdot}6_1$
HBr	0·0713	0·0895	$-1{\cdot}6_7$
HI	−0·1522	−0·0522	−9·6

[a] Data from: R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1965. [b] Molar scale. [c] Ref. 3 gives E°_m = 0·1672 V.

The nature of the solvation interactions will be elaborated in a later paper, together with a detailed discussion of extrapolation procedures and activity coefficients for solvents of high relative permittivity.

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